RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

DDT Plus PCB's in Blubber of Harbor Seals

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ABSTRACT

Samples of blubber from 13 harbor seals (Phoca vitulina richardii) *were collected in 1971 from San Miguel Island, Calif.; the Columbia River, Oreg.; Puget Sound, Wash.; and the Pribilof Islands, Alaska. Total amounts of DDT plus PCB's ranged from 380.7 to 2,359.9 ppm in five San Miguel Island seals; 459.4 to 1,620.0 ppm in two Puget Sound seals; 27.7 to 109.9 ppm in three Columbia River seals; and 6.8 to 27.8 ppm in three Pribilof Islands seals. There was no indication of loss of total DDT plus PCB's in three samples reanalyzed after 2 years in frozen storage.*

Introduction

Organochlorine pesticides have been found in seals in widespread parts of the world (*1,2*), but few data have been published on pesticides in harbor seals (*Phoca vitulina richardii*) from the eastern North Pacific Ocean. Up to 142 ppm DDE, 7.1 ppm DDD, and 2.6 ppm DDT were found in blubber from two harbor seals taken off central California (*3*). Up to 1,039 ppm total DDT and 145 ppm PCB's (polychlorinated biphenyls) were found in California sea lions (*Zalophus californianus californianus*) from San Miguel Island, Calif. (*4*), one of the areas sampled in this study. This report documents the amounts of DDT and its metabolites plus PCB's in the blubber of 13 harbor seals (*Phoca vitulina richardii*) collected in 1971 from four areas of the eastern North Pacific Ocean: San Miguel Island, Calif.; Columbia River, Oreg.; Puget Sound, Wash.; and the Pribilof Islands, Alaska.

Harbor seals of the subspecies *richardii* are nonmigratory and occur in the eastern North Pacific Ocean from Mexico to the Bering Sea. If food species preyed on by the seals do not migrate far, these seals might be used to locate geographical areas where organochlorine hydrocarbon levels are high. Harbor seals living off British Columbia feed near shore on demersal fish and octopus, although some migratory Pacific salmon (*Oncorhynchus* sp.) are eaten seasonally (*5*). Harbor seals feeding off Amchitka Island, Alaska, eat Atka mackerel (*Pleurogrammus monopterygius*) and octopus (*Octopus* sp) (*6*). A study of harbor seals in Washington showed that cods, flounders, Pacific herring, and sculpins made up 93 percent of the total diet. Squid and octopus make up another 6 percent (*7*). Harbor seals apparently feed on both migratory and nonmigratory species.

Sampling Procedures

All seals appeared to be in good health at the time of collection, except one seal from Washington which had apparently died from a deep laceration from a previous injury. Samples were collected by taking about 100 g of blubber from the belly area of each seal, near the midline and anterior to the mammaries. Blubber was

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selected for this study because organochlorine compounds are lipophilic (*1*). Samples were placed in new glass bottles and shipped frozen to the testing laboratory, WARF Institute, Inc., Madison, Wis.

Ages were estimated by counting layers of dentine in upper canine teeth (*8,9*). The error in assigning ages to harbor seals is not known. Body length was measured from the tip of the snout to the end of the tail, with the seal placed on its back.

Analytical Procedures

Samples of blubber were analyzed by gas-liquid chromatography for the following organochlorine compounds: aldrin, chlordane, endrin, heptachlor, heptachlor epoxide, methoxychlor, toxaphene, dieldrin, benzene hexachloride (BHC), PCB's, and the *o,p'* and *p,p'* isomers of DDE, DDD, and DDT. Only BHC, PCB's, and the *p,p'* isomers of DDE, DDD, and DDT were detected in 13 samples analyzed in 1971 and in 3 samples rerun in 1973. Confirmatory tests by use of thin-layer chromatography (*10*) on the rerun samples confirmed DDE, DDD, DDT, and PCB's, but not BHC. Levels of BHC will not be reported because of the negative confirmatory test.

To determine concentrations of the various organochlorine compounds, the entire 100-g sample of blubber was cut up while frozen, run through a hand food grinder, and transferred to ether-rinsed 4-oz glass jars. A random 5-g portion was placed in a tared 100-ml beaker and the weight was recorded. The sample was then dried at 40°C for 3 to 5 days, weighed for moisture content, and transferred to a 100-ml volumetric flask using petroleum ether. The blubber consisted almost entirely of fat and dissolved entirely in the petroleum ether. No weighable amounts of insolubles were found. Cleanup was carried out on a Florisil column following standard procedures (*11*). Next, the resulting solutions were concentrated to 10-15 ml and made to 25 ml with hexane. Sample solutions of 10 μl or less were injected into a Barber-Coleman Model 5360 gas chromatograph with an Sr90 electron-capture detector and the following instrument conditions:

Columns:	4-ft-by-4-mm glass packed with 5 percent DC-200 on gas chrom Q 80/100 (packed with 3 percent OV-17 on gas chrom Q 100/120 for BHC). An OV-17 + QF-1 column was added in 1973.
Temperature:	Detector 250°C; injector 230°C; column 210°C (180°C for BHC).
Carrier gas:	Nitrogen at a flow rate that gave *p,p'*-DDT a retention time of 6-8 minutes (12-14 minutes for BHC).

Peak heights were measured to quantitate organochlorine pesticide residues. Recovery rates ranged from 80 to 90 percent for all organochlorine compounds. Recoveries were run through the entire procedure, including the drying step. No corrections were made for recovery rates. The lower limits of detection were 0.02 ppm for DDE, DDD, and DDT, and 0.05 ppm for PCB's. Pesticide levels were only slightly higher on a fat basis than on a wet-weight basis, so results are reported here on a wet-weight basis only.

Aroclor 1254 was used as the standard for PCB's. Only the peak between DDT and DDD was used for estimation of PCB's, so the values for PCB's are not precise. Values for total DDT undoubtedly include some PCB's. To avoid possible errors, total DDT and PCB's were summed.

Because of high laboratory costs, only one sample was analyzed by the silicic acid method to separate DDT from PCB's (*12*). The blubber from this seal, a 176-cm male from San Miguel Island, had 2,110.0 ppm DDE, 3.98 ppm DDD, 96.1 ppm DDT, and 572.0 ppm PCB's. Total DDT plus PCB residues were 18 percent higher from the silicic acid method than were results from regular analyses. This difference is within the limits of analytical variability.

Glass bottles used to store the samples had paper lid-liners. The amounts of organochlorine compounds found in a sample of unused lid-liners would have had a maximum effect of 0.086 ppm total DDT plus PCB's. Because the additions, if they occurred, would have little effect on the observed values, data were not adjusted.

Results

Levels of total DDT plus PCB's ranged from 380.7 to 2,350.0 ppm (geometric mean 610.7) in San Miguel Island seals, 459.4 to 1,620.0 ppm (geometric mean 862.7) in Puget Sound seals, 27.7 to 109.9 ppm (geometric mean 62.5) in Columbia River seals, and 6.8 to 27.8 ppm (geometric mean 11.3) in Pribilof Islands seals (Table 1). Geometric means were computed because of the skewed distributions of the organochlorine compound residues. The organochlorine levels overlapped in San Miguel Island and Puget Sound seals, and in Columbia River and Pribilof Islands seals. Levels in the Columbia River and Pribilof Islands seals did not overlap the levels in San Miguel Island and Puget Sound seals. A one-way analysis-of-variance test shows that the mean total DDT plus PCB levels differed significantly between areas ($P<0.01$).

The Pribilof Islands are isolated from areas of high population and industrialization: the Columbia River drains large agricultural areas in Oregon, Washington, and Idaho; and San Miguel Island and Puget Sound are close to highly industrialized areas. Harbor seals taken near heavily populated and industrialized areas had the highest total DDT plus PCB levels, and seals

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TABLE 1.—*Total DDT[1] plus PCB's in blubber of harbor seals collected in 1971*

Location	No. of seals	Month collected	Age, yr	Length, cm	Moisture, %	Fat, %	Total DDT + PCB's (mg/kg; wet wt)	
							Geometric mean	Individual values
California: San Miguel Island	5	June	9-30–	153-176	0.9-1.4	96.6-99.2	610.7	380.7; 418.5; 435.5; 518.3; 2,350.0
Oregon: Columbia River	3	May	2-4	112-126	1.8-3.6	96.2-100.0	62.5	27.7; 80.4; 109.9
Washington: Puget Sound	2	June-August	1	95-119	2.4-5.0	90.5-95.1	862.7	459.4; 1,620.0
Alaska: Pribilof Islands	3	August	(2)	135-175	2.6-6.2	92.8-100.0	11.3	6.8; 7.1; 27.8

[1] DDE + DDD + DDT.
[2] Canine teeth lost.

taken from the most isolated area, the Pribilof Islands, had the lowest levels. However, larger samples are needed to verify these results. Variability due to sex and age could not be evaluated for these data because of the small sample sizes. Maximum residue levels occurred in male seals in each area, but the oldest seals did not have the highest total DDT plus PCB levels within an area.

After 2 years of frozen storage, two samples from San Miguel Island and one from the Pribilof Islands were reanalyzed. Total DDT plus PCB values were +18 percent, −16 percent, and −3 percent, respectively, of the original values. Results from the original and rerun samples are within the limits of analytical variability and indicate no significant changes in residue levels.

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LITERATURE CITED

(1) *Holden, A. V., and K. Marsden. 1967.* Organochlorine pesticides in seals and porpoises. Nature 216(5122): 1274-1276.

(2) *Sladen, W. J. L., C. M. Menzie, and W. L. Reichel. 1966.* DDT residues in Adelie penguins and a crabeater seal from Antarctica. Nature 210(5037):670-673.

(3) *Shaw, S. B. 1971.* Chlorinated hydrocarbon pesticides in California sea otters and harbor seals. Calif. Fish Game 57(4):290-294.

(4) *DeLong, R. L., W. G. Gilmartin, and J. G. Simpson. 1973.* Premature births in California sea lions: association with high organochlorine pollutant residue levels. Science 181(4105): 1168-1170.

(5) *Spalding, D. J. 1964.* Comparative feeding habits of the fur seal, sea lion, and harbor seal on the British Columbia coast. Bull., Fish. Res. Bd. Can. 46. 52 pp.

(6) *Kenyon, K. W. 1965.* Food of harbor seals at Amchitka Island, Alaska. J. Mammal. 46(1):103-104.

(7) *Scheffer, T. H., and C. C. Sperry. 1931.* Food habits of the Pacific harbor seal, *Phoca richardi*. J. Mammal. 12(3): 214-226.

(8) *Fiscus, C. H., G. A. Baines, and F. Wilke. 1964.* Pelagic fur seal investigations, Alaska waters, 1962. U.S. Fish Wildl. Serv. Spec. Sci. Rep. Fish. 475. 59 pp.

(9) *Laws, R. M. 1952.* A new method of age determination for mammals. Nature 169(4310):972-973.

(10) *Mulhern, B. M., E. Cromartie, W. L. Reichel, and A. A. Belisle. 1971.* Semiquantitative determination of polychlorinated biphenyls in tissue samples by thin layer chromatography. J. Ass. Offic. Anal. Chem. 54(3): 548-550.

(11) *U.S. Food and Drug Administration. 1968.* Pesticides analytical manual. Vol. 1. Sec. 211.15. Washington, D.C.

(12) *Armour, J. A., and J. A. Burke. 1970.* Method for separating polychlorinated biphenyls from DDT and its analogs. J. Ass. Offic. Anal. Chem. 53(4):761-768.

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